

Neuantrag auf Sachbeihilfe

PHD Proposal

Acronym:

February 15, 2016

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1 Background

1.1 Natural gas and aerosol emissions in Australia

The Australian landscape is largely uninfluenced by human activity. These environments are sources of naturally released trace gases which make up less than 1% of earth's atmosphere. Naturally occurring trace gases in the atmosphere can have a large impact on living conditions. They react in complex ways with other elements (anthropogenic and natural), as well as affecting various ecosystems upon which life depends. Natural emissions can drift over populous areas and influence local pollution levels in various ways. Ozone can be produced when some natural trace gases interact with pollutants from petrol combustion, and in the lower atmosphere ozone is a serious hazard that not only causes health problems (?), and billions of dollars worth of damage to agricultural crops (?), but also increases the rate of climate warming (?). Particulate matter in the atmosphere is also a major problem, causing an estimated 2-3 million deaths annually (????).

Natural emissions can also alter the radiative and particulate matter distribution of the atmosphere, complicating simulations and increasing uncertainty when not properly accounted for. The Australian outback includes large and diverse environments, which can have unique chemical sources. Much of the landscape outside of urban areas is undeveloped and sparsely inhabited. In Australia most long term air quality measurements are performed in or near large cities. However, estimates of atmospheric gas and particulate densities and distributions over much of the rest of the continent are uncertain and lack in-situ measurements.

One source of information which covers the entirety of Australia is remote sensing performed by instruments on satellites which overpass daily, recording reflected solar radiation (and emitted terrestrial radiation). These can be used to quantify the abundance of several chemical species as well as estimate their vertical distribution over the land. While satellite data is effective at covering huge areas, these data have their own limitations and uncertainties. Satellite data does not have high temporal resolution, is subject to cloud cover, and generally does not have fine horizontal or vertical resolution.

The existence of satellite data covering remote areas provides an opportunity to develop more robust models of global climate and chemistry. Natural emissions from areas with little anthropogenic influence and no ground based measurements

characterise the majority of Australian land mass (?). Understanding of emissions from these areas is necessary to inform national policy on air pollution levels. Satellite data allow us to verify large scale model estimates of natural emissions. These measurements can be used to improve models, inform national policy, and predict harmful events.

This thesis will combine satellite and ground based atmospheric measurements with chemical transport modelling to clarify the impact of Australian natural emissions on atmospheric composition and chemistry. In the following subsections the main atmospheric species to be analysed in this thesis are discussed. Then the satellite and modelling techniques to be used will be examined.

1.2 Tropospheric ozone

Ozone is a toxic trace gas which increases mortality rates when populations are exposed for extended periods of time. The amount of global premature deaths per year due to atmospheric ozone exposure has recently been estimated at ~150-470 thousand (??). Long term effects of ozone overexposure increase the risk of respiratory disease and may also increase other cardiopulmonary risks (?).

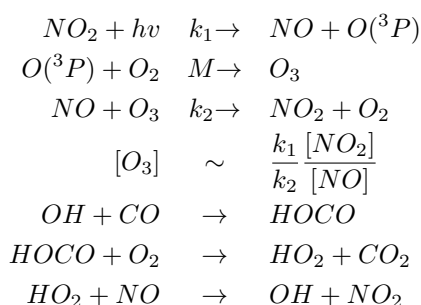
The Ambient Air Quality (AAQ) National Environment Protection Measure (NEPM), which is the Australian framework for air quality measurement and reporting aiming for “adequate protection of human health and well-being” has set national standards and benchmarks for reporting. The NEPM covers six chemical groups including Ozone (O_3), and the benchmarks are shown in figure 1.

The primary source of ozone in the lower troposphere is chemical formation following emissions of precursor gases, including VOCs, and NO_X . Globally the greatest sources of NO_X include fossil fuel combustion (~50%), biomass burning (~20%), lightning, and microbial activity in soils (?). Estimates using CHASER (a global Chemical Transport Model (CTM)) constrained by measurements from two satellites as well as the in-situ measurements taken through LIDAR and aircraft (INTEX-B) put global tropospheric NO_X emissions at 45.4 TgN yr^{-1} in 2005 (?).

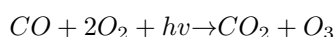
The majority of this chemical formation is due to photochemical oxidation of carbon monoxide (CO), methane (CH_4), and other Volatile Organic Chemicals (VOCs) in the presence of nitrogen oxides ($NO_X \equiv NO + NO_2$) (?).

While photochemical production is the dominant source, stratosphere to troposphere transport (STT) of ozone is also important and climate change may drastically increase this quantity (?). Ozone-rich air mixes irreversibly down from the stratosphere during certain meteorological conditions (??). In the extra-tropics, STTs most commonly occur during synoptic-scale tropopause folds (?) and are characterised by tongues of high Potential Vorticity (PV) air descending to low altitudes. PV is a metric which can be used to determine whether a parcel of air is stratospheric, based on its local rotation and stratification. These tongues become elongated and filaments separate from the tongue which mix into tropospheric air. Stratospheric ozone brought deeper (lower) into the troposphere is more likely to affect the surface ozone budget and tropospheric chemistry (??).

Photolysis of NO_2 forms $NO + O(^3P)$, which combines with O_2 to form O_3 , leading to reaction with NO to form $NO_2 + O_2$. These reactions reach a steady state where O_3 is proportional to the ratio between NO_2 and NO (?). The following formulae show an example of this with CO, however, similar reactions occur for many VOCs:



where k_1 and k_2 are reaction rates, and $h\nu$ represents photons. The balance of these reactions is:



Isoprene (C_5H_8) is a precursor to ozone through radical oxidative chemistry. Isoprene in the atmosphere reacts rapidly with hydroxyl radicals (OH) and then O_2 to form peroxy radicals (RO_2). These react with nitrogen oxides and can lead to ground-level ozone formation similarly to the CO reaction listed prior.

Together formaldehyde (HCHO) and NO_2 regulate tropospheric oxidation capacity through O_3 production, as well as being health hazards. The HCHO/ NO_2 ratio can be used to determine whether surface O_3 is NO_2 or VOC limited (?). If O_3 is NO_2 limited then an increase in NO_2 will increase O_3 levels while an increase in HCHO will not, and vice versa when O_3 is HCHO limited. NO_2 is a common pollutant in populated areas, released primarily by combustion in power generation and transport. Outside of cities in Australia, VOCs and NO_x are emitted from biogenic sources, although lightning, and biomass burning (most clearly in the Northern Territory) also play a role (??).

The amounts of tropospheric ozone from STTs and photochemical production are estimated to be around 550 and 5100 Tg yr^{-1} , respectively. The main ozone removal processes are chemical destruction and dry deposition, respectively removing 4650, 1000 Tg yr^{-1} from the the troposphere (?).

NEPM standards and goals specified in Schedule 2 of the AAQ NEPM

Pollutant	Averaging period	AAQ NEPM standard (maximum concentration)	AAQ NEPM goal (maximum number of allowable exceedences)
Carbon monoxide	8-hour rolling average	9.0 ppm	1 day a year
Nitrogen dioxide	1-hour average	0.120 ppm	1 day a year
	1-year average	0.030 ppm	None
Photochemical oxidants – as ozone	1-hour average	0.100 ppm	1 day a year
	4-hour rolling average	0.080 ppm	1 day a year
Sulfur dioxide	1-hour average	0.200 ppm	1 day a year
	1-day average	0.080 ppm	1 day a year
	1-year average	0.020 ppm	None
Particles as PM ₁₀	1-day average	50.0 µg/m ³	5 days a year
Lead	1-day average	0.50 µg/m ³	None
Particles as PM _{2.5} ¹	1-day average	25.0 µg/m ³	Gather sufficient data nationally to facilitate a review of the Advisory Reporting Standard
	1-year average	8.0 µg/m ³	

¹ Reporting standard only

Figure 1: NEPM standards taken from National Environment Protection Council annual report 2012-2013 (?).

1.3 Isoprene and formaldehyde (HCHO)

Methane and isoprene each comprise around a third of the yearly global total emission of VOCs. However, methane is relatively long lived (years) and is well mixed in the atmosphere while isoprene levels are very volatile and spatially diverse due to a life time of around an hour. Estimates put global isoprene emission at roughly 550 Tg yr⁻¹ (?), emitted mostly by trees and shrubs during the day. Isoprene is hard to measure directly due to its short lifetime and weak spectral absorption, instead formaldehyde (HCHO) is often used as a proxy (?).

Biogenic isoprene emissions are far greater than anthropogenic emissions of VOCs (?). The lack of accuracy in BVOC emissions estimates has a large effect on determining with confidence the sources and distribution of pollutants including ozone and organic aerosols. Accuracy in VOC measurements is important: it has been shown that even the diurnal pattern of isoprene emissions has an effect on modelling ground level ozone (?). These uncertainties could explain why models of HCHO over Australia are poor at reproducing satellite measurements (?).

A widely used estimate of global isoprene emissions is the Model of Emissions of Gases and Aerosols from Nature (MEGAN). MEGAN uses leaf area index, forest canopy modelling, and plant functional type emission factors to simulate terrestrial isoprene emissions. Emission factors represent quantities of a pollutant released to the atmosphere through an associated activity. For example, an emission factor for isoprene within a forest would include the requirement of sunshine and suitable temperature. ? estimates that the Australian outback is among the world's strongest isoprene emitter with forests in SE Australia having emission factors greater than 16 mg m⁻² h⁻¹ (see figure 2).

These emissions factor estimates are not well verified as there is little coverage of isoprene (or other BVOC) emissions measurements over Australia. However, comprehensive coverage of one of the products of isoprene chemistry in the atmosphere over Australia exists in the form of satellite measurements. Satellites recording reflected solar spectra use Differential Optical Absorption Spectroscopy (DOAS) to measure various trace gases in the atmosphere, including formaldehyde (HCHO). HCHO levels in the continental boundary layer are generally dominated by chemical formation due to VOC emissions, which are largely isoprene (?). Using satellite data from 2004 (see section 1.5) we have a broad measure of seasonal and inter-annual variability of HCHO over Australia. These records can be compared with modeled estimates of HCHO and used as a proxy to estimate isoprene emissions. This has been done in North America, South America, and Africa, with satellite and aircraft data combined for validation (?).

The methodology for calculating VOCs from HCHO is laid out in ?, and takes into account the expected lifetime and reaction rates of the precursor VOCs and HCHO. Assuming HCHO is produced quickly from short-lived intermediates we get

$$VOC_i k_i \rightarrow Y_i HCHO$$

Where Y_i is HCHO yield per C atom (a measure of how much HCHO will form per gram of C from a VOC within a system). Then assuming a steady state of atmospheric HCHO (Ω molecules cm⁻²) produced by oxidation of VOCs (VOC_{*i*}) and no

horizontal transport:

$$\Omega = \frac{1}{k_{HCHO}} \sum_i Y_i E_i$$

Where i indexes a chemical species, and E_i is emission fluxes (C atoms $cm^{-2}s^{-1}$).

Inferring the VOC emissions then requires estimates of the HCHO yield (Y_i) which can be attained via modelling as layed out in ?.

During low NO_x conditions, the precursor HCHO has a longer lifetime (days). This allows horizontal transport to occur and complicates the algorithms. Horizontal transport 'smears' the HCHO signal so that source location would need to be calculated using windspeeds and loss rates. In high NO_x environments where HCHO has a lifetime on the order of 30 minutes HCHO can be used to map isoprene emissions with spatial resolution from 10-100 kms. For conditions where VOCs have a lifetime of days determining the major HCHO contributors requires a complex inversion to map HCHO columns to VOC emissions.

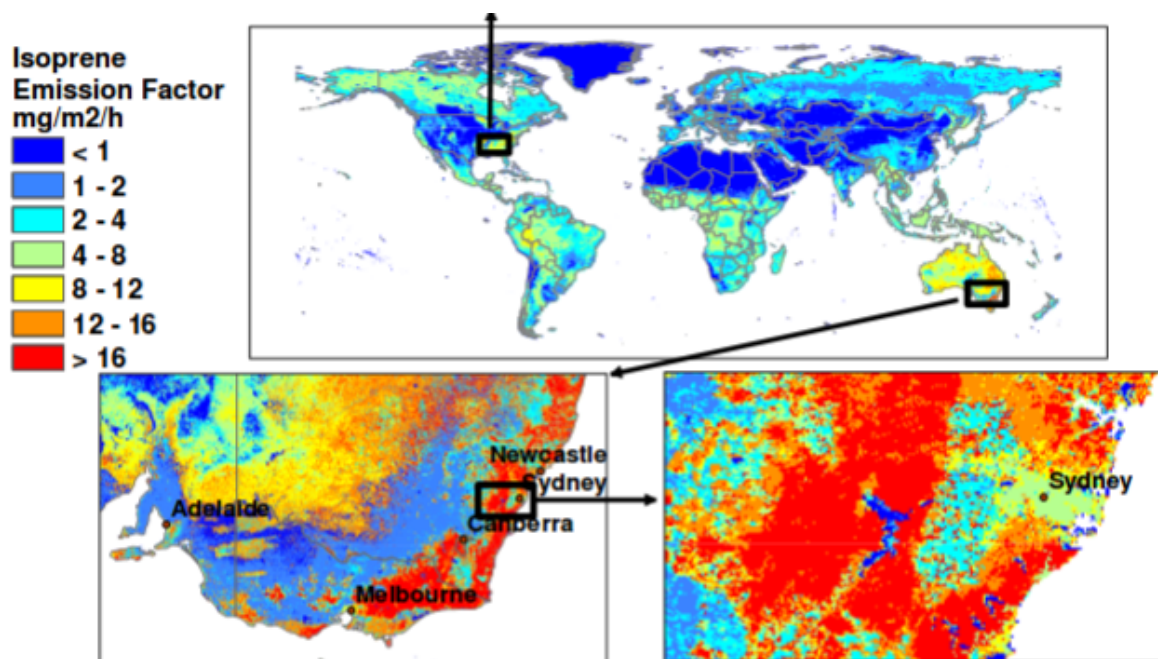


Fig. 2. Global distribution of landscape-average isoprene emission factors ($mg \text{ isoprene } m^{-2} h^{-1}$). Spatial variability at the base resolution ($\sim 1 \text{ km}$) is shown by regional images of the southeastern U.S. and southeastern Australia.

Figure 2: Part of a figure from ? showing global isoprene emission factors.

1.4 Dust

Australia is the greatest source of dust in the southern hemisphere producing around 120 Tg yr^{-1} (?), however model validation and analysis over Australia is relatively scarce with more focus applied to the northern hemisphere (??). Atmospheric dust has many direct effects including reduced surface insolation (incoming solar radiation), mineral transfer to remote ocean regions, and health degradation in populated areas (?). The indirect effects of dust are not fully understood, and many models still struggle to explain the atmospheric cycling of dust at larger scales (?).

Australian dust emissions involve various weather conditions, convolving the ENSO cycle with flooding, droughts, and winds. Rivers and rain build up the particulate matter in many areas, these are referred to as fluvial deposits. Fluvial deposits in the Eyre basin increase the dust base load, which will only have mobility during suitable dry weather conditions. These deposits are saltated and transported by strong winds(?). Saltation is the process of small particles agitating larger particles, causing them to become airborne.

Synoptic scale measurements of dust concentrations in Australia are made by the Bureau of Meteorology (BOM) and can be used to estimate dust transport caused by large storms. Single storms have been estimated to move up to 2.5 Tg of dust off shore in a single day. Yearly dust emissions in Australia are somewhere between 10 and 110 Tg yr^{-1} . These estimates exemplify the large variability in Australian annual dust transport.

Dust plays a large role in the oceanic carbon cycle, as dust is a major source of oceanic iron (Fe) deposition. Some regions in the ocean are high in nutrients, but low in chlorophyll (HNLC), due to a lack of Fe. Oceanic carbon cycling is a complex system in which Fe is a limiting factor, required by plankton in order to fix atmospheric nitrogen into a more bioavailable form such as ammonia. Atmospheric deposition into the oceans is a very poorly constrained variable in global models (?).

Model estimates of trace element oceanic deposition are required to quantify the atmospheric impact due to a dearth of in situ measurements in remote open ocean regions.

Measurements of dissolved iron (DFe) at very low concentrations like those found in surface ocean waters are very easily contaminated, which has contributed to the fragmentary and scarce nature of DFe ocean data sets (?). Recent analysis of the US Climate Variability and Predictability (CLIVAR)-CO₂ Repeat Hydrography Program predicted total deposition flux with uncertainty at a factor of 3.5 (?). Some headway has been made with the recent GEOTRACES program which has several transects of the major oceans and measures trace elements over multiple depths including Al, Ba, Cu, Cd, Fe, Mn, Ni, Pb, and Zn.

Total iron (TFe) emissions from dust and combustion sources are estimated (by average of several global models) at approximately 35 Tg yr⁻¹ and 2 Tg yr⁻¹ respectively. A two fold increase in Fe dissolution may have occurred since 1850 due to increased anthropogenic emissions and atmospheric acidity. This increase may revert by 2100 due to the affects of emission regulations (?). Dust, TFe and DFe have strong temporal and spatial variability, with changes having most impact upon HNLC regions.

Another environmental impact of dust is its contribution to fine particulate matter in the atmosphere. Several studies have shown that long term exposure to fine particulate matter (PM2.5) increases mortality. Estimates of yearly premature deaths related to PM2.5 are ~ 2-3 million (????). These estimates are made using global atmospheric models or model ensembles to quantify population exposure before applying epidemiological models to estimate the increased death rates. The main source of uncertainty in premature death rates arises from the difference and uncertainties between and within the atmospheric models.

Dust affects global climate change through direct radiative forcing. Uncertainties in the atmospheric dust concentrations make accurate determination of radiative forcing from other sources more difficult (?).

1.5 Satellites

Several satellites provide long term trace gas observations with near complete global coverage, including the ERS-2 launched in April 1995 which houses the GOME ultraviolet and visible (UV-Vis) spectrometer, the AURA launched in July 2004 which houses the OMI UV-Vis spectrometer, the MetOp-A and B launched in October 2006 and September 2012 respectively both housing a GOME-2 UV-Vis spectrometer. These satellites are on Low Earth Orbit (LEO) trajectories and overpass any area up to once per day. They record near nadir (or almost vertical) reflected spectra between around 250-700 nm split into spectral components at around 0.3 nm in order to calculate trace gases including O₃, NO₂, and HCHO. An example of a spectrum retrieved from the GOME-2 instrument is given in figure 3.

Formaldehyde (HCHO) is often used as a proxy to estimate isoprene emissions (??). Satellites can use DOAS techniques with radiative transfer calculations on solar radiation absorption spectra to measure column HCHO (eg: ?). Several public data servers are available which include products from the satellites just mentioned, including NASA's Mirador (<http://mirador.gsfc.nasa.gov/>) and the Belgian Institute for Space Aeronomy (IASB-BIRA) Aeronomie site (<http://h2co.aeronomie.be/>).

DOAS techniques with radiative transfer calculations use various parts of a solar radiation absorption spectra to measure trace gases through paths of light. DOAS methods can be heavily influenced by the initial estimates of a trace gas profile (the a priori) which is often produced by modelling, so when comparing models of these trace gases to satellite measurements extra care needs to be taken to avoid introducing bias from unrealistic a priori assumptions. A way to remove these a priori influences in order to compare models and satellites is through the satellite's averaging kernel, which is a measure of the sensitivity of the instrument to the trace gas's radiance at various heights multiplied by the sensitivity of the DOAS technique's forward radiative transfer model (RTM) to the amount of trace gas at various heights near the a priori (?).

The RTM used in DOAS techniques is based on Beer's law relating the attenuation of light to the properties of the medium it travels through. Beer's law states that $T = I/I_0 = e^{-\tau}$ with T being transmittance, τ being optical depth, and I, I₀ being radiant flux received at instrument and emitted at source respectively. Using $\tau_i = \int \rho_i \beta_i ds$ gives us:

$$I = I_0 \exp \left(- \sum_i \int \rho_i \beta_i ds \right)$$

Where i represents a chemical species index, ρ is a species density (molecules per cm³), β is the scattering and absorption cross section area (cm²), and the integral over ds represents integration over the path from light source to instrument. The forward RTM used for satellite data products also involves functions representing extinction from Mie and Rayleigh scattering, and the efficiency of these on intensities from the trace gas under inspection, as well as accounting for various atmospheric parameters which may or may not be estimated (e.g. albedo). Rayleigh and Mie scattering describe two kinds of particle effects on radiation passing through a medium. Rayleigh scattering is heavily wavelength dependent, and is the dominant form of scattering from particles up to roughly one tenth of the wavelength of the light. Mie scattering is more dominant from larger particles, and has less wavelength dependence.

To convert the trace gas profile from a reflected solar radiance column (slanted along the light path) into a purely vertical column requires calculations of an air mass factor (AMF) due to the non strict path of light measured by the instrument. The AMF is normally a scalar value for each horizontal grid point which will equal the ratio of the total vertical column density to the total slant column density. This value should also account for instrument sensitivities to various wavelengths at various altitudes, and is unique for each trace gas under consideration.

Instruments including MODIS on board the AQUA and TERRA satellites are able to determine aerosol optical depth (AOD), a measure of atmospheric scatter and adsorption. An AOD of under 0.05 indicates a clear sky, while values of 1 or greater indicate increasingly hazy conditions. This is an important atmospheric property allowing us to track dust storms and pollution events as well as determine where measurements from other instruments may be compromised by high AOD. Satellite measured AOD requires validation by more accurate ground based instruments like those of AERONET which uses more than 200 sun photometers scattered globally.

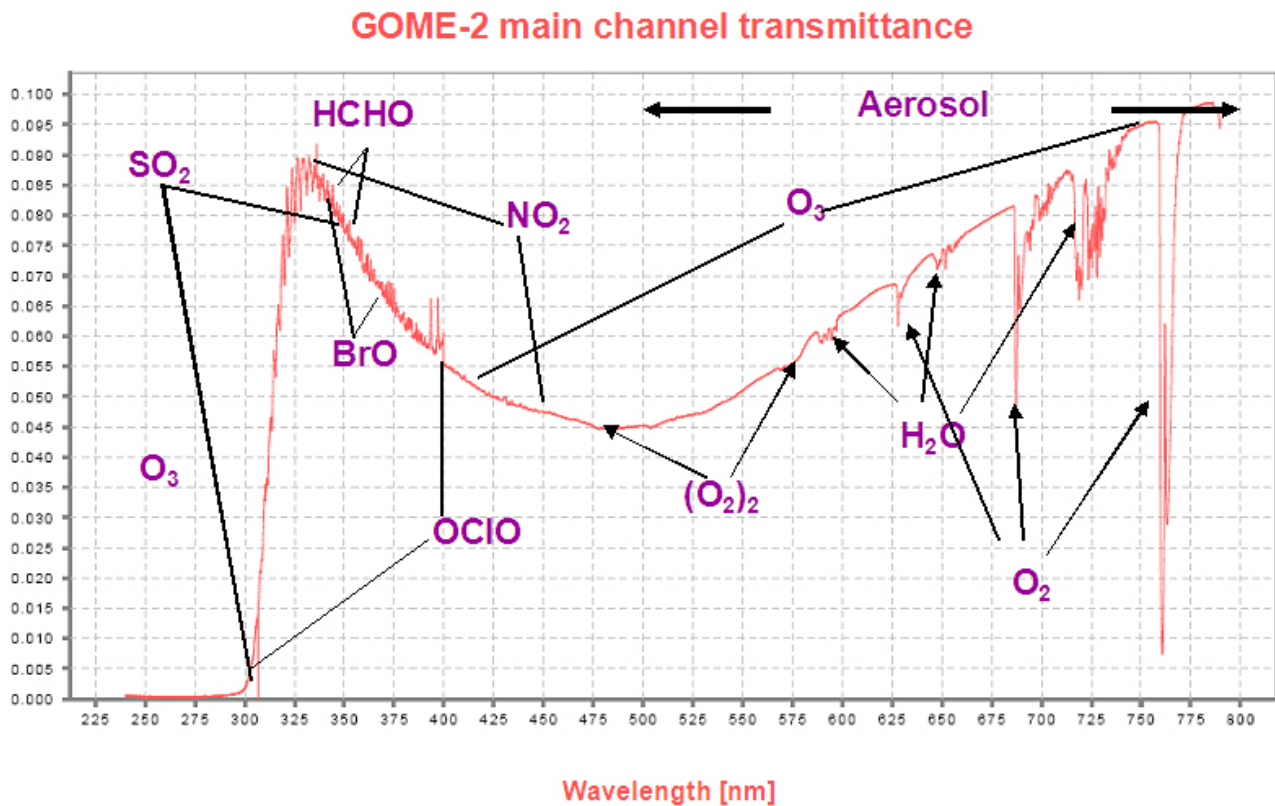


Figure 3: An example spectrum showing interferences used for species concentration measurements by GOME-2. Image by EUMETSAT and ESA (?).

1.6 Chemical Transport Models

Chemical Transport Models (CTMs) simulate production, loss, and transport of chemical species. This is generally calculated using one or both of the Eulerian (box) or Lagrangian (puff) frames of reference. CTMs normally solve the continuity equations simultaneously with chemical production and loss for chemicals under inspection. The continuity equations describe transport of a conserved quantity such as mass, which, solved together with production and loss of a chemical forms the basis for a CTM. This basis enables a record of the chemical densities and transport over time as a model runs. The general continuity equation links a quantity of a substance (q) to the field in which it flows and can be described by the formula:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = \sigma$$

where ρ is density of q in the field, t is time, ∇ is divergence, \mathbf{j} is the flux (the amount of q per unit area per unit time entering or leaving the field), and σ is the generation of q per unit volume per unit time. Note that σ can be positive or negative due to sources and sinks.

The type of model best suited to modelling the entire earth uses the Eulerian frame of reference, where the atmosphere is broken up into 3-D boxes with densities and transport calculated and stored for arbitrary sequential steps in time at each location. The mass balance equation must be satisfied in any realistic long term box model and is as follows:

$$\begin{aligned} \frac{dm}{dt} &= \sum \text{sources} - \sum \text{sinks} \\ &= F_{in} + E + P - F_{out} - L - D \end{aligned}$$

where m is mass of a chemical, E and D are emission and deposition, P and L are production and loss, and F is chemical transport in and out, as shown in figure 4. Many chemical species interact with each other through production and loss. Any

large chemical model will solve this mass balance equation over highly coupled arrays of partial differential equations which can be complex and time consuming.

GEOS-Chem is a well supported global, Eulerian CTM with a state of the science chemical mechanism, with transport driven by meteorological input from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO). GEOS-Chem simulates more than 100 chemical species from the earth's surface up to the edge of space (0.01 hPa) and can be used in combination with remote and in-situ sensing data to give a verifiable estimate of atmospheric gases and aerosols. It was developed, and is maintained, by Harvard University staff as well as users and researchers worldwide. Several driving meteorological fields exist with different resolutions, the finest at 0.25 by 0.3125° horizontally at 5 minute time steps with 72 vertical levels.

Combining satellite data with model outcomes provides a platform for the understanding of natural processes to be tested now and into the future over Australia and anywhere with few in-situ measurements. Due to the low availability of in-situ data covering most of the Australian continent, a combination of the models with satellite data may provide improved understanding of emissions from Australian landscapes. Improved emissions estimates will in turn improve the accuracy of CTMs, providing better predictions of atmospheric composition and its response to ongoing environmental change.

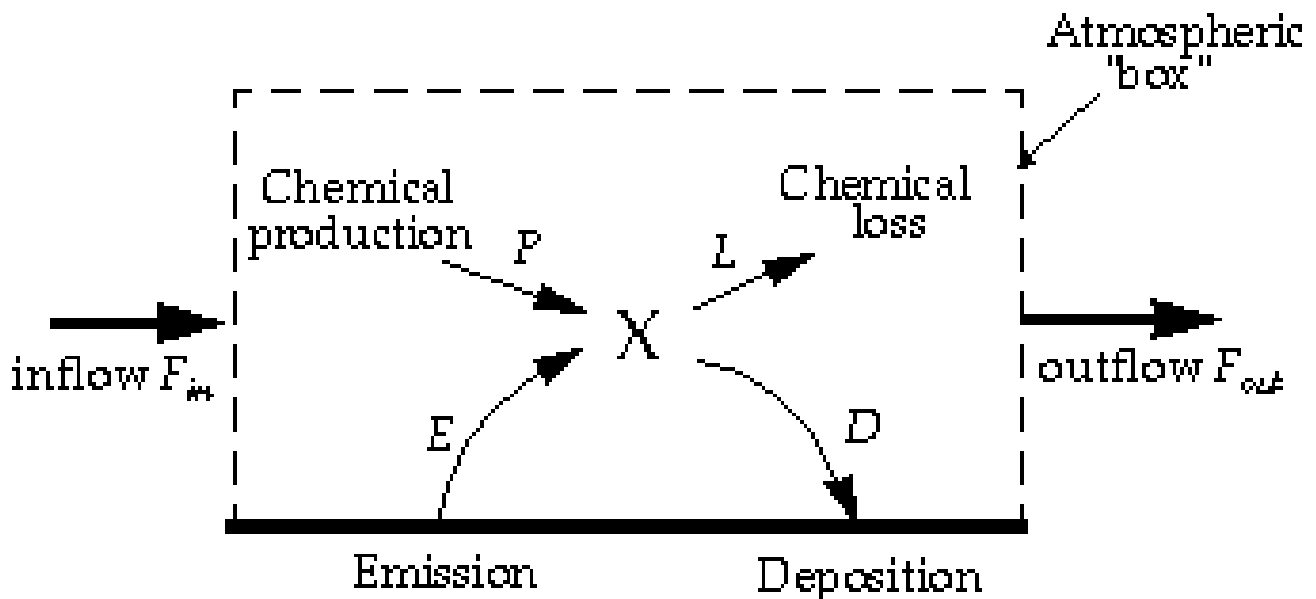


Figure 4: Standard box model parameters, image taken from ?.

2 Research Proposal

2.1 Aims

1. To determine the impact and causes of stratosphere to troposphere ozone transport (STT) using ozonesondes and ECMWF weather reanalysis data. Work on this aim is almost complete, hopefully I can submit a paper to ACP as first author in early 2016.
2. To quantify Australian isoprene emissions using satellite data and the GEOS-Chem model. This will be commenced soon.
3. To attribute Australian ozone influence from isoprene, and STT sources over particular sites using in-situ data and model output.
4. To improve the GEOS-Chem model by allowing increased resolution over Australia.
5. To quantify Australia's dust emissions and transport modelled by GEOS-Chem and validate against in-situ and remote sensing data.

2.2 Stratospheric Ozone transport

2.2.1 Preliminary Results

The impact of stratospheric ozone on the troposphere is dependent on weather, season, temperature, and many other factors. To understand potential drivers for ozone pollution at the earth's surface there is a need to quantify how often and how

intensely various ozone events occur. Here, records of ozone profiles provided by the Department of the Environment are used to determine how often stratospheric ozone descends into the troposphere.

Ozonesondes are weather balloons with an attached instrument which measures ozone concentrations roughly every 100m up to around 30km. These ozonesondes provide a vertical profile of ozone. A Fourier bandwidth filter can remove components of a line based on the components frequency. For example a noisy ozone profile can be 'cleaned' by removing the high frequency components, while growth of ozone with altitude in the profile can be removed as a low frequency component. With a Fourier bandwidth filter used on ozone profiles over Davis, Macquarie, and Melbourne we quantitatively determine instances of Stratosphere to Troposphere Transport events (STTs).

The vertical profiles of ozone volume mixing ratio are linearly interpolated to a regular grid with 20m resolution up to 14km altitude and are then bandpass filtered so as to retain perturbations on altitude scales between 0.5km - 5km. The choice of band limits is set empirically, however it should be noted that to define an STT event, a clear increase above the background ozone level is needed. Setting the vertical scale limit of 5 km removes seasonal-scale column ozone trends as well as the slow ozone increase which occurs from the ground up to the tropopause. This removes the need to subtract the seasonally averaged column ozone when analysing the perturbation columns. The ozone perturbation profile is examined between 2 km above the surface (to avoid surface pollution events) and 1 km below the tropopause (to avoid the sharp transition to stratospheric air). Perturbations above the 99 th percentile (locally) of all ozone levels are then classified as STT events.

Ozone profiles from 2004 until 2013 show clear STT influence on about 15% of the days which are measured: with 36, 50, 73 events recorded from 240, 390, 456 ozonesonde profiles respectively for Davis, Melbourne, and Macquarie. In addition to this STTs are shown to have seasonal cycles with more frequent occurrences in late summer at both Macquarie and Melbourne. The amount of ozone transported to the troposphere is estimated conservatively through integration over the excess ozone concentration around the concentration peak which exceeds the event threshold (see figure 5). The result of this integration shows an increase in tropospheric ozone of ~3% due to STTs, with maxima ~11%.

The filtered ozone profiles automatically account for seasonal ozone differences as the perturbation at desired scales ignores the baseline ozone concentration. An examination of the seasonal behaviour of the tropospheric ozone according to the ozonesondes can be seen in Figure 6.

In order to look at the weather systems behind STTs synoptic scale pressure data is taken from the European Centre for Medium-Range Weather Forecasts (ECMWF) Re-Analysis Interim data set (ERA-I). STTs can often occur due to cut-off low and low front pressure systems and examples of each of these weather patterns which coincide with an STT determined from our algorithm gives a clear indication that the algorithm can be used robustly. One of these case studies involves a record breaking storm over Melbourne on the third of February 2005 and is shown in figure 7. This figure represents a massive low pressure system directly above Melbourne, with winds moving clockwise around the storm (arrows). Also shown is the ozonesonde's vertical profile of ozone, temperature, and relative humidity as it was released and ascended through the middle of the storm.

2.2.2 STT Discussion

Most of the analysis for this work has been completed, with a couple of issues to explain before being published to ACP. Foreign and local influence of transported pollution or smoke plumes needs to be discussed, as well as the reversibility of the STT events.

Some work has been done on long range influence of pollution from the tropics over southern mid-latitudes starting with ? The impacts should be relatively small, especially over Macquarie and Davis which are at high southern latitudes.

Using local weather patterns from ERAI we can infer that most of our detected ozone events are occurring during conditions conducive to irreversible transport. Further analysis of the weather data may be warranted however it will remain to be done outside of this project.

This work will also be useful in extra analysis and validation of the GEOS-Chem simulation of ozone over Australia and the near southern ocean.

2.3 Australian isoprene emissions

2.3.1 Preliminary Results

Preliminary analysis has been performed on satellite HCHO data showing seasonal trends in Australian regions. Additionally several satellite measurements and column totals have been intercompared. SCIAMACHY suffers from poor measurement quality south of 30°S and is not reliable for our purposes, however GOME-2 and OMI records cover Australia Completely.

An example of an intercomparison of Summer (Dec-Feb) HCHO measurements for three satellites can be seen in figure 8.

Finally a preliminary comparison of the FTIR spectrometer retrieval with a GEOS-Chem modelled column of HCHO through the use of averaging kernel de-convolution is completed.

2.3.2 Isoprene Discussion

Filtering out the non biogenic sources of HCHO over Australia will be performed similarly to (?), modified to suit Australia.

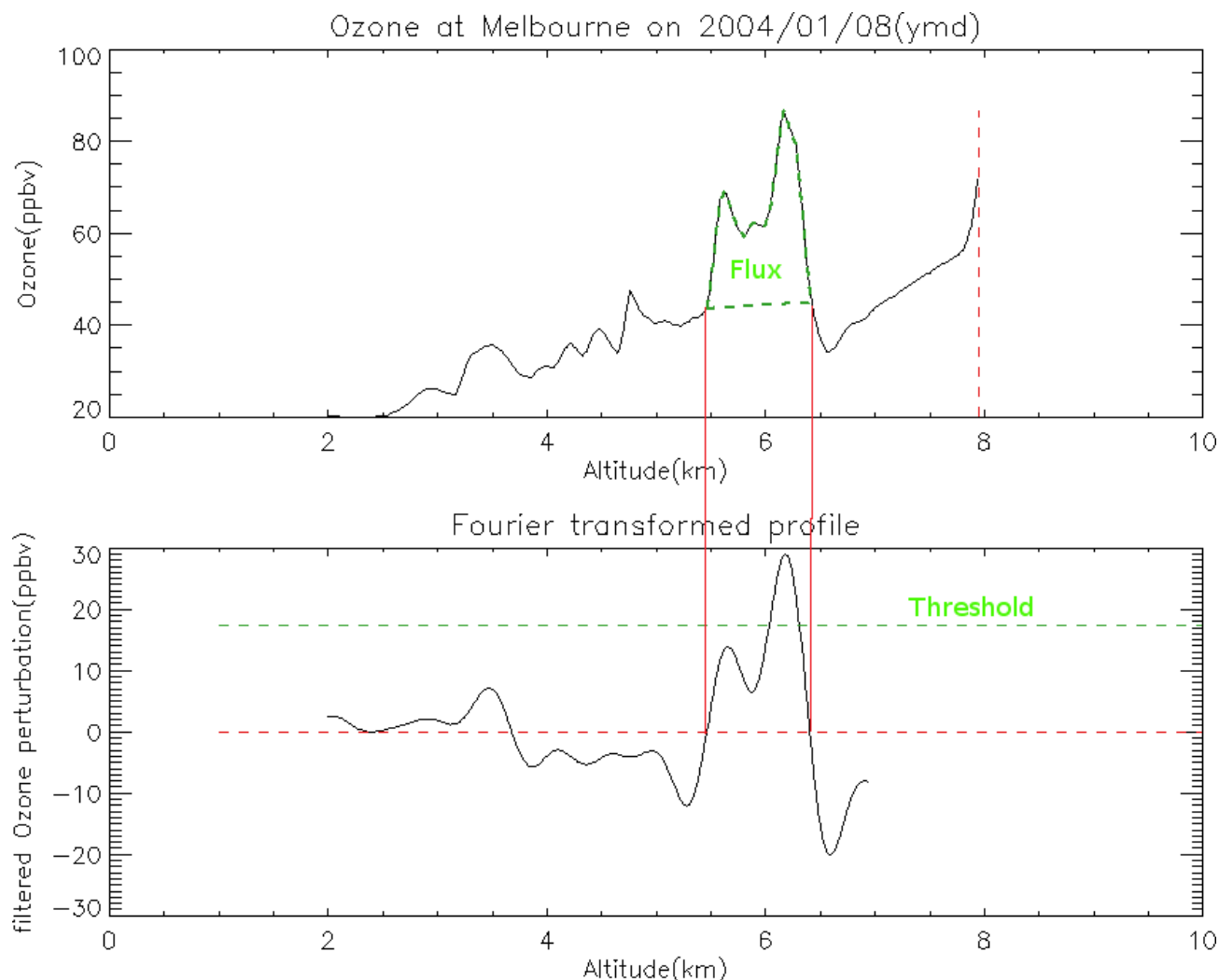


Figure 5: Top: example of a classified STT with the marked area showing how estimation of ozone imported from the stratosphere is calculated. Bottom: the Fourier bandwidth filtered ozone profile used to classify STTs and quantify transported ozone.

Determination of purely biogenic emissions of HCHO from satellite-based observations is possible by filtering out biomass burning using the fire counts and AOD. The AATSR, Aqua, and Terra satellites have fire counts which can be used to determine when HCHO is caused by burning or smoke plumes, as well as accounting for other anthropogenic emissions (gas flaring).

Applying the formulas laid out in section 1.3 will produce estimates of isoprene emissions using HCHO as a proxy. The effect of uncertainties due to factors like smearing and a priori measurement uncertainty on the quality of isoprene emissions will then be determined.

Finally with satellite based isoprene emissions estimates we will undertake two tasks. A direct comparison of these estimates against in situ measurements, such as the Measurements of Urban, Marine and Biogenic Air (MUMBA). A results comparison of GEOS-Chem using simulations based on the created isoprene emissions estimates against commonly used inventories such as those created by MEGAN.

This method of inference has been used successfully in several countries including North America(?), South America (?), and Western Africa (?).

The outcomes from the emissions analysis will contribute to planning for the COALA aircraft campaign which may take place in 2018/2019.

2.4 Dust

2.4.1 Preliminary Work

Australian dust emissions are largely estimated using global models which are not tuned for Australian conditions (??).

Using GEOS-Chem model version 9.02 and comparing against both AERONET and Community DustWatch Information Interface (CoDii) in situ data allows a model validation in an area which is largely estimated due to lack of ground based measurements.

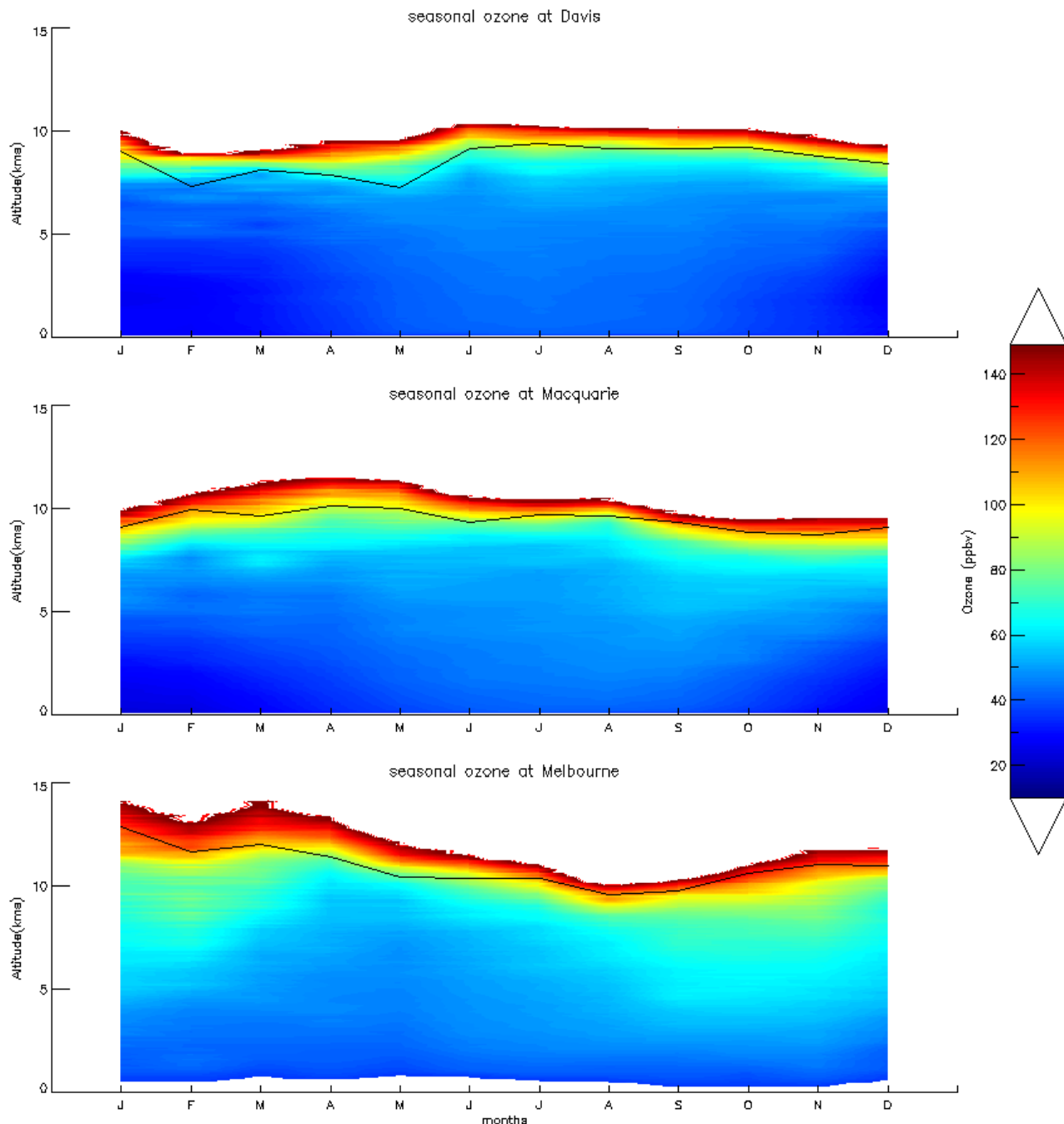


Figure 6: Seasonal ozone concentrations up to 15km over Davis, Macquarie, and Melbourne, tropopause shown as a black line.

Running GEOS-Chem at 2x2.5 resolution, using offline GEOS-5 meteorological fields and DEAD dust mobilisation provides a simulation of global dust emission, deposition, and transport. The Dust Entrainment and Deposition (DEAD) dust mobilisation scheme is based on surface wind speeds to the third power, implemented by ?. We only model emission, deposition, and transport of dust and carbon, allowing a fast runtime. Running the full chemical model to see if dust was affected by other tracers found only negligible differences (in the order of 10^{-5} percent). With 2004 as the spin up year, monthly average columns of sources and sinks and AOD are simulated until November 2012.

There are very few in-situ measurement stations recording AOD which are predominantly dust related. Two which do exist are within AERONET, Tinga Tingana and Birdsville, and a direct comparison between these sites can be seen in figure 9. These records of AOD show a fairly close match to the model, with much of the observed variability captured, especially at Birdsville.

Looking at the seasonal distribution of dust emissions and deposition also shows agreement with the AERONET dust dominated sites. While Australian summers are can be hot and dry, the majority of dust activity occurs in September and October, as can be seen in figure 10

A comparison between 45 separate CoDii dust watch sites showed little correlation to modelled dust concentrations. CoDii

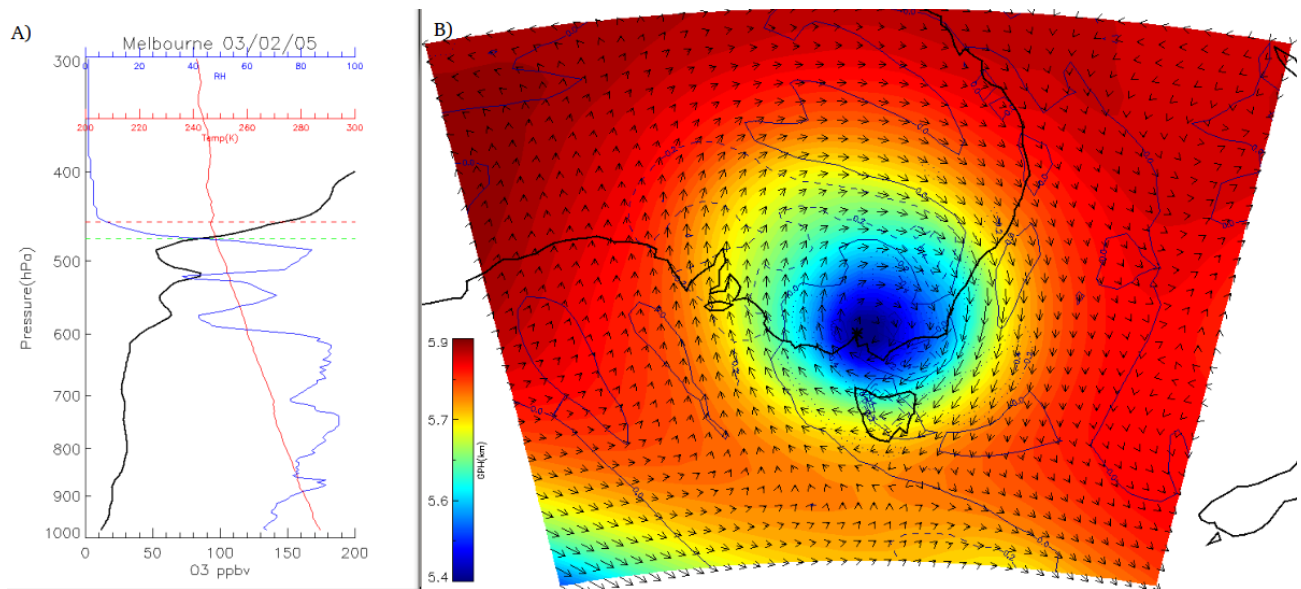


Figure 7: A) Ozonesonde profile of ozone (black) relative humidity (blue) and temperature (red) from the surface up to 300hPa (around 9km). B) ERA-I geopotential height (GPH: comparable to pressure) and wind (arrows) at 500hPa (around 5.5km).

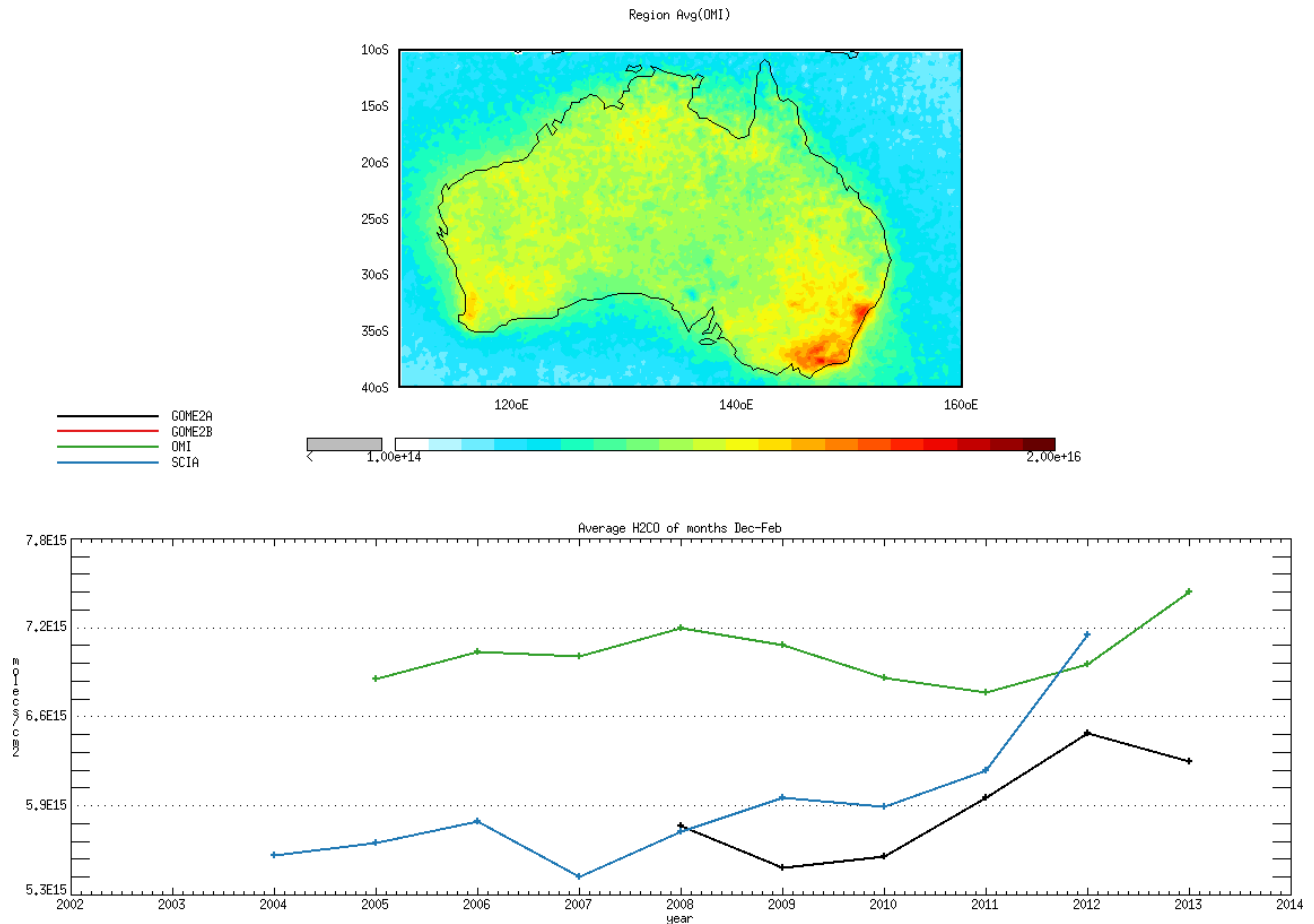


Figure 8: Formaldehyde Summer average measured over the pictured region for GOME2 (black), OMI (green), and SCIAMACHY (blue).

sites are single point measurements, looking at just the surface dust concentration, while the AERONET represents AOD over the whole column which is more directly comparable to the model. Similarly to AERONET, satellite AOD represents column totals and may be a more apt source of model verification.

Several model inaccuracies occur due to the low resolution of the GEOS-Chem simulation. A horizontal grid does not

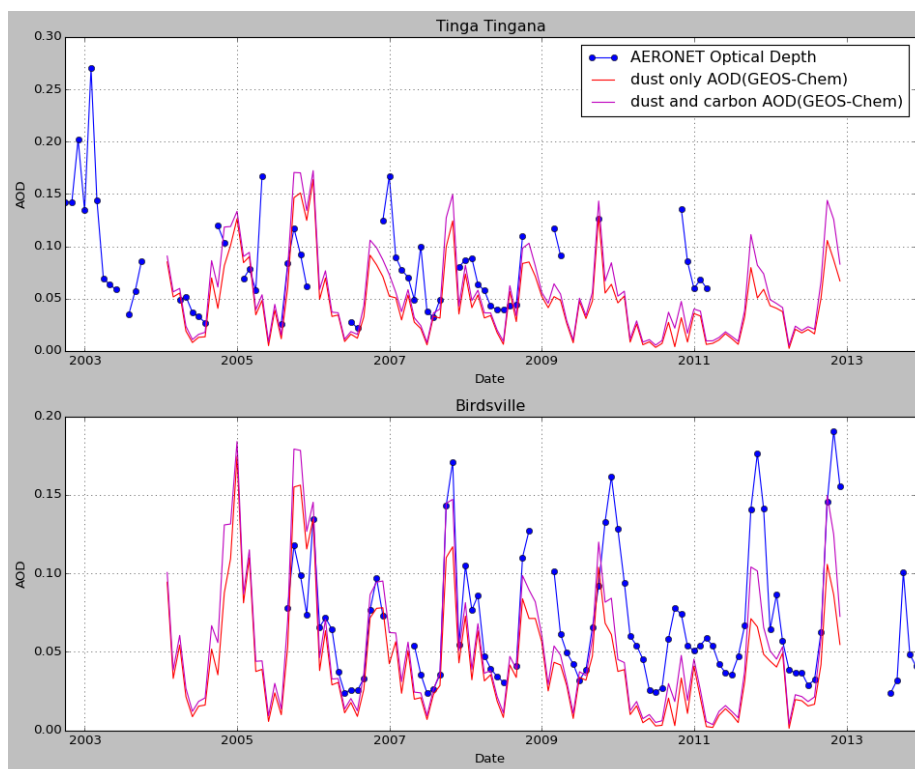


Figure 9: AOD from GEOS-Chem compared against AERONET measurements taken at Tinga Tingana and Birdsville.

capturing the sub grid wind speed distribution (?), which leads to an underestimation of dust production. Another problem lies in comparing area averages against in-situ data. Using area averages limits the model's ability to capture small scale dust events and smears out the effect of large events.

The simulation from 2005 until 2012 recorded an average of almost 50 Tg yr^{-1} of dust emitted from Australia, with about 37 Tg yr^{-1} deposition, suggesting more than 10 Tg yr^{-1} of dust is exported offshore. Within the simulation 30 Tg yr^{-1} of Australia's emitted dust is sourced from the Eyre basin.

Australian dust could play a large role in oceanic primary production through algal blooms in the southern ocean. Using modelled estimates of deposition with and without the Eyre basin dust source allows a minimal bound estimate of Australia's direct contribution to the total southern oceanic dust deposition.

2.4.2 Dust Discussion

This work has been presented as a poster at the 7th international GEOS-Chem meeting (IGC7). With improved model resolution (see section 2.5) it is expected that dust emission accuracy will improve. A comparison of simulations at different resolutions against both in situ and satellite measurements of AOD and dust concentrations across Australia should show an improvement in model estimations of these attributes.

An analysis of possible meteorological drivers of dust export will also be undertaken.

If improvements to the model can be shown to improve the correlation with in-situ measurements then it would become worthwhile to publish.

2.5 Improved GEOS-Chem resolution over Australia

2.5.1 Preliminary Work

A preliminary understanding of the mechanics required to both build and run the model at various resolutions has been achieved through active modelling and participation in IGC7.

2.5.2 GEOS-Chem Resolution Discussion

Higher resolution modelling over Australia will allow for both improved validation with in situ measurements, and regional scale simulation analysis. An increase in maximum resolution from $2^\circ \times 2.5^\circ$ to $0.25^\circ \times 0.3125^\circ$ will be implemented. Dust simulation in particular can be greatly improved with finer surface wind resolution.

During this PhD the GEOS-Chem model will be improved by allowing enhanced horizontal resolution over Australia and possibly NZ. This has been done already over China (??), North America (?), Europe (?), and the Amazon (?).

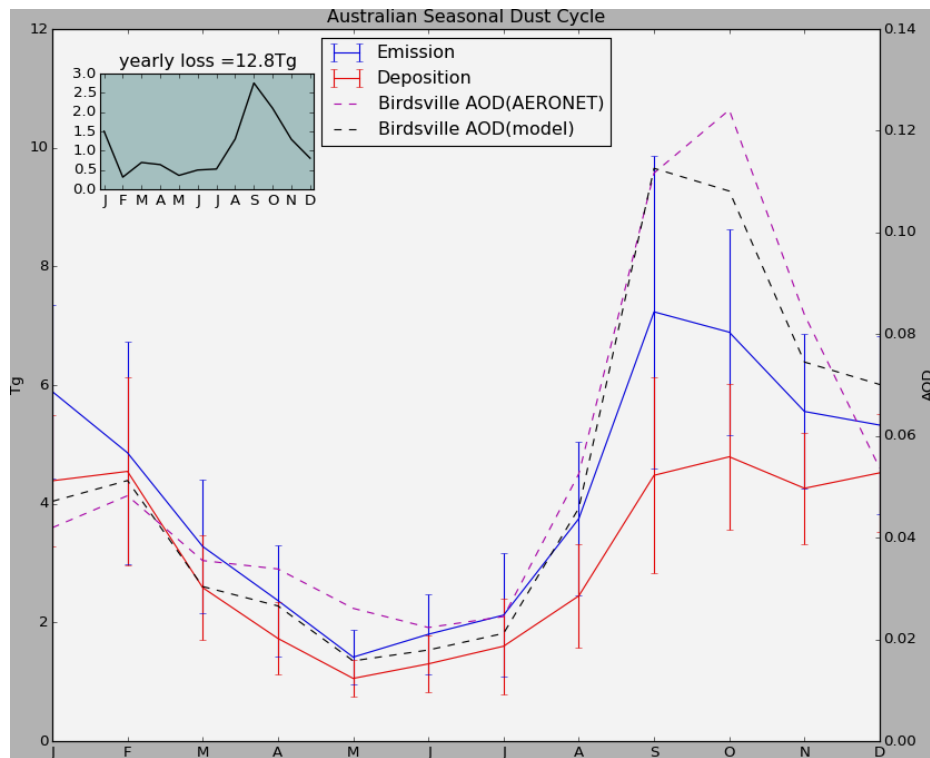


Figure 10: Seasonal dust emission (solid blue) and deposition (solid red) averaged across Australia. Vertical lines are one standard deviation. Dotted lines show the Birdsville measured and simulated seasonal AOD averaged across all available years.

After determining the desired spatial and temporal boundaries for improved resolution, raw data will be downloaded, verified, and re-gridded using existing code (developed for other regions by the GEOS-Chem support team). To ensure that we have an acceptable inventory for Australian emissions existing inventories from state EPAs may need to be patched together.

Finally, emissions data needs to be reworked over the domain, ensuring emissions factors are maintained. This last requirement may be eased by the new HEMCO module implemented within the Earth System Model Framework (ESMF) (compatible with GEOS-Chem v10) which recalculates emissions on any user specified grid.

2.6 Ethics, Intellectual Property and Safety

This research project involves no humans or animals and does not require ethics approval.

Intellectual Property rights to data products released by the satellites considered within this thesis are free to use and publish, with a citation of sources requested.

2.7 Resources

The Center for Atmospheric Chemistry (CAC) already has access to proprietary software which is required to compile the GEOS-Chem model, which is itself open source. CAC has access to the University of Wollongong's high performance computing servers as well as the The National Computational Infrastructure, both of which allow high demand computational tasks such as running and developing GEOS-Chem.

3 Future schedule

3.1 2016

Initially sorting the HCHO satellite data into manageable formats and determining an appropriate filtering scheme for Australia will take place. Running the simulation and then comparing satellite and model HCHO will follow.

The methods for comparison are mathematically complex in order to account for various reflectances and extinction effects as well as instrument sensitivities and understanding and utilising these concepts will take some time.

Following these tasks, the inversion of HCHO will take place in order to estimate isoprene emissions. The results from this will contribute to planning for a field campaign to take place in south eastern Australia in 2017 focused on biogenics as well as a possible aircraft campaign in 2018 led by the National Center for Atmospheric Research (NCAR).

Finalising ozone analysis from the in-situ ozonesonde measurements and submitting this as a paper to the journal of Atmospheric Chemistry and Physics (ACP) will also take place early in 2016

3.2 2017

Setting up a nested grid within the GEOS-Chem model will allow higher resolution simulations over Australia. The new resolution will need to be tested and compared against benchmark simulations in order to verify that the implementation has not caused any undesired effects. This will involve collaboration with several people involved in GEOS-Chem development and the National Environmental Science Programme (NESP) Clean Air and Urban Landscapes Hub.

Thesis writing will be an ongoing task throughout the course of this PhD.

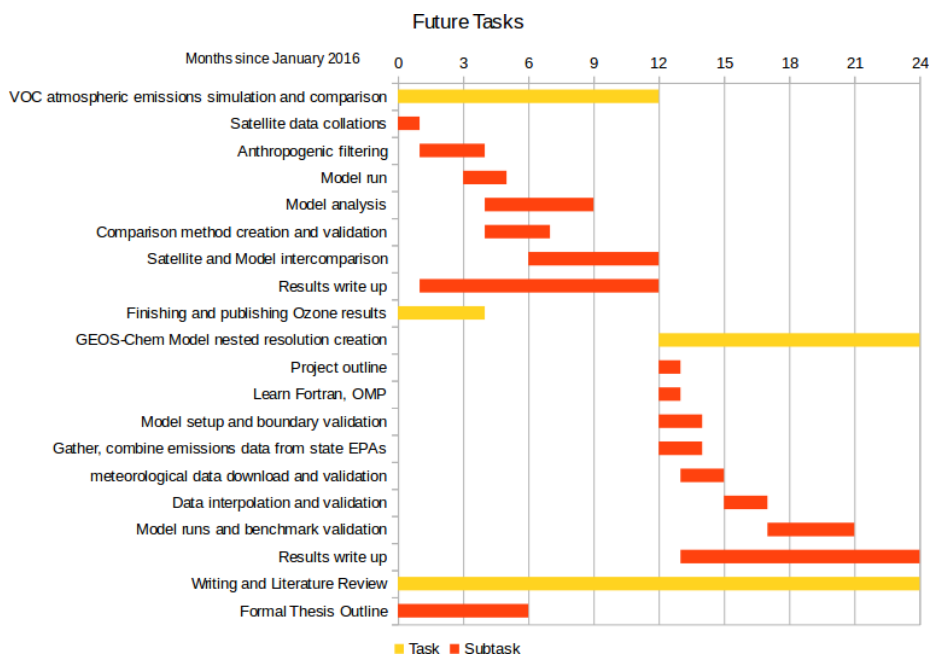


Figure 11: Future work schedule